

TITLE: IMPROVED EFFICIENCY IN THE SULFUR DIOXIDE - IODINE
HYDROGEN CYCLE THROUGH THE USE OF MAGNESIUM OXIDE

MASTER

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IMPROVED EFFICIENCY IN THE SULFUR DIOXIDE - IODINE HYDROGEN CYCLE THROUGH THE USE OF MAGNESIUM OXIDE*

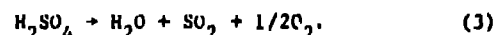
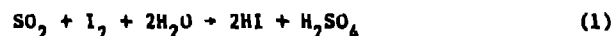
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ABSTRACT

The reaction of iodine with dry magnesium oxide and magnesium sulfite hexahydrate was studied experimentally as a possible means of improving the efficiency of the sulfur dioxide-iodine cycle. When no extra water was introduced, the maximum product yield was 57% obtained at 423 K. With excess water vapor, a nonporous plug was formed which prevented complete reaction. In the second case, maximum yield was 62% measured at 433 K showing that added water does not increase reaction products. This reaction gives an alternate route for producing hydrogen from water via the sulfur dioxide-iodine process.

INTRODUCTION

The sulfur dioxide-iodine thermochemical hydrogen cycle (General Atomic Cycle) can be summarized by the following reactions:



It is, at this time, one of the more fully developed thermochemical cycles with a thermal process efficiency of 30% (1). The major reasons that the efficiency is not higher are the two energy intensive steps of drying and decomposing H_2SO_4 and also drying HI for which phosphoric acid is used.

In order to circumvent these two problems, we propose to carry out reactions (1) and (3) in stages using MgO to decrease the energy requirements. Thus, the relevant chemical changes can be summarized:



In this way, it should be possible to minimize the moles of water needed for complete reaction by using steam in reaction (6) so there are no solution steps.

The major potential disadvantage of this system involves the experimental difficulties associated with handling solids. However, in this particular sequence, the solids can remain in one place while they are subjected to different temperatures and different gas

flows. It has been found recently that another solid sulfate, bismuth sulfate, can be decomposed at rates suitable for a commercial process (2).

Thermodynamic Considerations

From the Ellingham Diagrams shown in Fig. 1 [the thermodynamic data is taken from Ref. (3)], it is seen that, in the presence of steam, at temperatures above 540 K any MgI_2 formed should be hydrolyzed directly to HI and MgO. Also at 540 K, the thermal decomposition of HI is already favored, so, when equilibrium is obtained about 15% decomposition will have occurred. Kinetically, the establishment of this equilibrium is slow, especially in the absence of catalytic surfaces (4). The heat requirements for the cycle are shown:

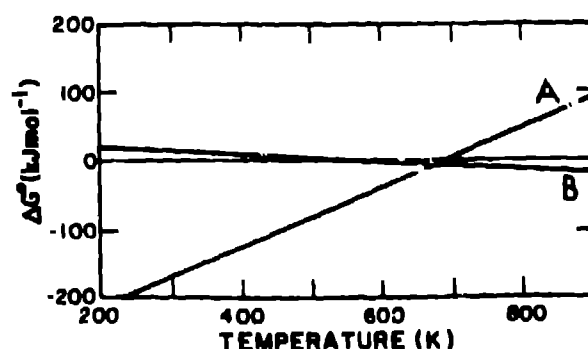
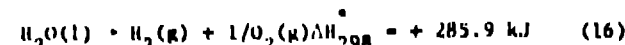
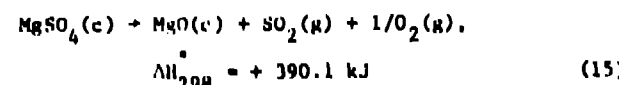
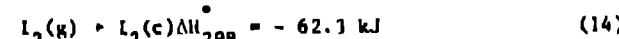
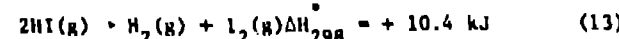
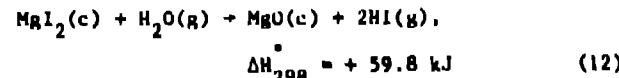
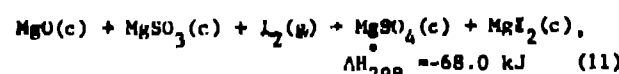
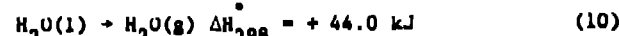
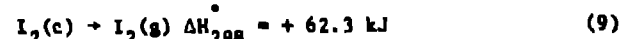
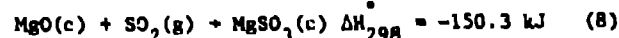


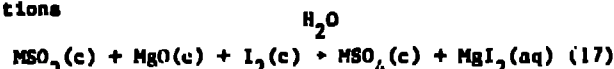
Fig. 1. Ellingham diagrams for Reaction 5-A and Reaction 6-B.

*Work performed under the auspices of the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

This gives a figure of merit of 0.50. If it proves possible to carry out reactions (11) and (12) concurrently, then this figure will increase to 0.56. If it is further assumed that the exothermic steps can furnish the heat for the lower temperature endothermic steps, then the only heat that need be supplied is for MgSO_4 decomposition. Thus, the figure of merit is further increased to 0.73.

Chemical Considerations

It has previously been established (5) that the reactions

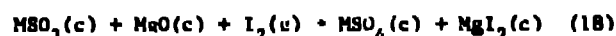


$$\text{where } M = \text{Mg}, \Delta H_{298}^\circ = -333.1 \text{ kJ}$$

$$M = \text{Ca}, \Delta H_{298}^\circ = -255.7 \text{ kJ}$$

$$M = \text{Ba}, \Delta H_{298}^\circ = -265.7 \text{ kJ}$$

occur readily both in dilute aqueous solution, and when $M = \text{Ca}$, 73% of the reaction occurs at a concentration of 4.0 mol l^{-1} . It has also been shown (6) that when $M = \text{Mg}$, it is unnecessary to separate the products prior to their hydrolysis and thermal decompositions, since the temperatures of the two reactions are separated by 500 K. Thermodynamically, these reactions can also proceed in the absence of water:



$$\text{where } M = \text{Mg}, \Delta H_{298}^\circ = -68.0 \text{ kJ}$$

$$M = \text{Ca}, \Delta H_{298}^\circ = -106.4 \text{ kJ}$$

$$M = \text{Ba}, \Delta H_{298}^\circ = -119.1 \text{ kJ}$$

Therefore, we set out to study the conditions under which reaction (18) will proceed. Although we consider here just the case of magnesium sulfite, we hope to extend these studies to include calcium, barium, and lanthanum sulfites.

RESULTS AND DISCUSSION

A thermogravimetric analysis was performed on $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$. The temperature range for loss of moles of water is shown in Table 1. Above 603 K, SO_2 was evolved and was complete by 823 K when a heating rate of $20^\circ \text{ min}^{-1}$ was used.

Table 1 Temperature Range for Loss of Water from $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$. (Heating Rate 20 K/min).

Temperature (K)	Moles of Water Lost
343 - 378	1
378 - 398	2
398 - 413	3
413 - 443	4
443 - 468	5
468 - 603	6

Initially, to study reaction (18) we passed dry I_2 through a mixture of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ and MgO at various temperatures. The results, indicating partial reaction, are shown in Table 2. I_2 will not react with MgO (7) and we found that neither will SO_2 up to 574 K. The water of hydration performs a significant role in the reaction. Maximum yield was obtained when about 2 moles of water of hydration were present. The yield drops sharply at higher temperature. The reaction took about 10 min, the time for the I_2 to pass through the solid bed. Therefore, the reaction is fast albeit in-

complete. The experiment performed at the lowest temperature was unique in this series, since it proved impossible for all the I_2 to pass through the solids as a nonporous plug was formed, accounting for the low yield.

Table 2 Reaction of I_2 Vapor with MgSO_3 and MgO .

$$\text{MgSO}_3 \cdot 6\text{H}_2\text{O} = 9.8 \times 10^{-3} \text{ M}, \text{MgO} = 9.8 \times 10^{-3} \text{ M},$$

$$\text{I}_2 = 11.8 \times 10^{-3} \text{ M}$$



Temperature K	MgSO_4 $\times 10^{-3} \text{ M}$	% Reaction
383	0.76	8
403	4.85	49
423	6.40	67
448	6.16	63
473	3.66	38
523	3.22	33
573	2.96	30

Since, in all cases, the reaction was incomplete, the experiments were repeated, passing both I_2 and water vapor through the solids. These results are shown in Table 3. For the two lower temperature experiments, the reaction was limited by the formation of a nonporous solid plug which prohibited gases being passed through it. This was not true at 573 K but the overall product yield was low.

Table 3 Reaction of I_2 and H_2O with MgSO_3 and MgO .

$$\text{H}_2\text{O} = 277.5 \times 10^{-3} \text{ M. Conditions as in Table 2.}$$

Temperature K	MgSO_4 $\times 10^{-3} \text{ M}$	% Reaction
433	6.07	62
523	2.65	26
573	0.93	10

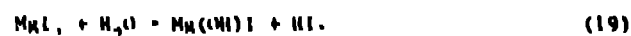
In order to see whether the observed nonporosity was dependent on the amount of water vapor, the experiments were repeated using less water vapor and these results are shown in Table 4. Partial inhibition to gas flow was observed and yields obtained were very similar to those in Table 3.

Table 4 Reaction of I_2 and H_2O with MgSO_3 and MgO .

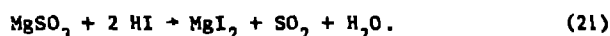
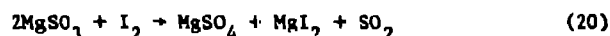
Conditions as in Table 2.

Temperature K	H_2O $\times 10^{-3} \text{ M}$	MgSO_4 $\times 10^{-3} \text{ M}$	% Reaction
423	13.8	5.15	55
423	27.8	5.52	56
523	27.8	2.89	29

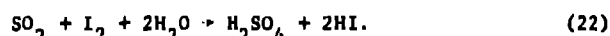
The measured amount of iodide formed was less than that of sulfate due to its solubility in acetone (8). Further, iodide was found in the water insoluble fraction of the solid products, which is due to $\text{Mg}(\text{OH})\text{I}$ from the x-ray powder diffraction pattern (6). This is an intermediate in the hydrolysis of MgI_2 :



HI was found in the water through which the exit gases were passed in a small relatively invariant amount. Both Mg(OH)I and HI accounted for no more than 3% each of reaction products in all cases. The low amount of HI formed, which was approximately equivalent to the Mg(OH)I found, shows that little SO_2 was evolved even though it is conceptually possible through the following reactions:



Any SO_2 formed was removed either by absorption on MgO , or, which is more likely by reaction with I_2 :



The HI would be present in the water through which the exit gases were bubbled and would result in higher iodide analyses than in Mg(OH)I . This was not found indicating little SO_2 evolution.

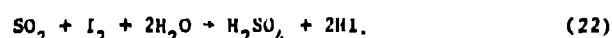
Any HI evolved, therefore, may react preferentially with MgO :



Instead of with MgSO_3 .

At temperatures greater than 540 K where the reverse of reaction (12) is favored, the results indicate low overall reaction and no enhanced HI formation. Thus it appears that, for optimal yields, if this approach is adopted, reaction (18) should take place around 423 K, followed by an increase in temperature and excess water to hydrolyse MgI_2 . This temperature increase must be sufficient to obtain porosity of the reactant solids (~ 573 K).

However, as the reaction yields do not reach 100%, and as the approach described sidesteps the issue of SO_2 reacting with MgO , an alternative approach was investigated. If SO_2 , I_2 , and H_2O were mixed prior to a MgO bed, then the fluids passing through the bed would be mainly H_2SO_4 and HI:



The MgO bed acts a medium to separate HI and H_2SO_4 :



Possibly some hydrolysis of MgI_2 will occur. Separation takes place by hydrolysing MgI_2 around 600 K and decomposing MgSO_4 at about 1200 K.

Therefore, preheated H_2SO_4 and/or HI were passed through a MgO bed; the results are given in Table 5.

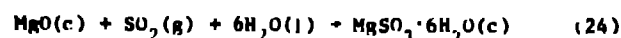
For the case of H_2SO_4 alone the reaction was nearly complete since H_2SO_4 is still a liquid at 383 K (bp 411 K). This is untrue for HI. The extent of the reaction was diminished due either to in situ hydrolysis of MgI_2 or to a diffusion limited rate since a gas/solid reaction was taking place. When a mixture of gases was used sulfate formation was decreased. The overall yields were found to be lower than in the previous approach which involves the prior formation of MgSO_3 .

Table 5 Results of passing HI (55%) and or H_2SO_4 (96%) through MgO at 383 K.

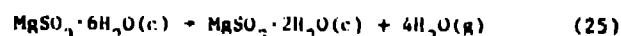
MgO $\text{Mx}10^{-2}$	H_2SO_4 $\text{Mx}10^{-2}$	HI $\text{Mx}10^{-2}$	Results $\text{Mx}10^{-2}$
9.0	9.0	----	7.8 anh. MgSO_4 (86%) 1.1 MgO 0.7 unreacted H_2SO_4 passed through MgO
3.8	---	4.0	1.4 anh. MgI_2 (35%) MgO residue
8.2	2.7	5.4	1.0 anh. MgSO_4 (37%) 6.8 MgO trace MgI_2 (4%)
3.9	1.4	2.7	0.5 anh. MgSO_4 (37%) 2.4 MgO - 40% MgI_2

Formation of $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ is the crucial precursor to reaction (18). It can be formed (9) by bubbling SO_2 through an aqueous slurry of MgO . Since $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ is relatively insoluble the solid mixture of MgO and $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ can be dried once the SO_2 uptake is such that half the oxide has been sulfited.

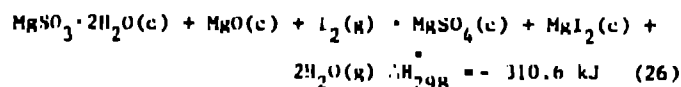
In reality, reactions (8) and (11) should be modified to include the energies of hydration and dehydration:



$$\Delta H_{298}^\circ = -194.5 \text{ kJ}$$



$$\Delta H_{298}^\circ = +229.2 \text{ kJ}$$



$$\Delta H_{298}^\circ = -310.6 \text{ kJ}$$



$$\Delta H_{298}^\circ = -43.8 \text{ kJ}$$

There is sufficient heat liberated in (26) to fuel the lower temperature dehydration (25). Thus hydrate formation, while enabling the cycle steps to be carried out as in the original hypothesis, do not result in any overall drop in the figure of merit.

CONCLUSIONS

No advantage is gained by using additional water for reaction (18). The optimal yield (6/2) was obtained at 423 K when between 2 and 3 moles of water per MgSO_3 still remained. This is insufficient water to hydrolyse MgI_2 , and thus subsequent MgI_2 hydrolysis must be carried out at a high enough temperature to keep the solid bed porous - as found at 573 K. Side reactions involving the evolution of SO_2 do not take place. Thus these reactions may provide an alternative route for hydrogen production from water via the SO_2 - I_2 process.

EXPERIMENTAL

$\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ (City Chemical Corp.) was purified by mixing with water to remove any sulfate present before drying at 343 K and the residual sulfate estimated gravimetrically (7.22). MgO (Mallinkrodt) and $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ were mixed and placed on a glass frit in the

center of a pyrex tube (i.d. 2.3 cm), inside a vertical tube furnace. I_2 (and H_2O) were vaporized and passed through the tube in a stream of argon in about 10 min. The solid products were analyzed by first removing the excess I_2 , using p-xylene and acetone. MgI_2 , as well as I_2 , is soluble in acetone, so that the extent of reaction was measured by sulfate analysis of the water soluble fraction using standard gravimetric procedures (10) after boiling the acidified solution to remove any soluble sulfite. Some iodide was also found (3%) in the water through which the gases were passed after leaving the reaction tube. Solid reaction products were identified by x-ray powder diffraction patterns. The thermogravimetric analysis was carried out on a Dupont 900 Thermal Analyzer.

ACKNOWLEDGEMENTS

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